

Simplistic Coulomb forces in molecular dynamics: Comparing the Wolf and shifted-force approximations

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This paper compares the Wolf method to the shifted forces (SF) method for efficient computer simulation of isotropic systems interacting via Coulomb forces, taking results from the Ewald summation method as representing the true behavior. We find that for the Hansen-McDonald molten salt model the SF approximation overall reproduces the structural and dynamical properties as accurately as does the Wolf method. It is shown that the optimal Wolf damping parameter depends on the property in focus, and that neither the potential energy nor the radial distribution function are useful measures for the convergence of the Wolf method to the Ewald summation method. The SF approximation is also tested for the SPC/Fw model of liquid water at room temperature, showing good agreement with both the Wolf and the particle mesh Ewald methods; this confirms previous findings [Fennell & Gezelter, *J. Chem. Phys.* **124**, 234104 (2006)]. Beside its conceptual simplicity the SF approximation implies a speed-up of a factor 2 to 3 compared to the Wolf method (which is in turn much faster than the Ewald method).

I. INTRODUCTION

In molecular dynamics simulations the force evaluation consumes by far the most computational resources. For relatively short-ranged interactions like van der Waals interaction¹ it is common to introduce a cutoff radius r_c such that if the distance between a particle pair exceeds r_c , the particles do not interact². This truncation allows for different optimization methods like inclusion of cell and neighbor lists²⁻⁴, which increase computational performance considerably. Traditionally, the pair potential is simply truncated and shifted such that it is zero at r_c ²⁻⁴. This does not affect the force acting between particles at distances below r_c , and if r_c is sufficiently large, the fluid properties are virtually unaffected by this approximation. In fact, it has been shown^{1,5} that keeping merely the short-ranged, purely repulsive part of the van der Waals interaction can account for the fluid structure even near the critical point where correlations are long ranged. The truncated and shifted potential approximation ensures continuity of the potential energy, but introduces a discontinuity in the force at r_c , leading to energy drift for long simulation times⁶. To overcome this one can instead apply a truncated and shifted force (SF) approximation², which has superior numerical stability⁶. Beside the numerical stability, it was recently shown by Toxvaerd and Dyre⁶ that for highly dense fluids the SF method allows for very small cut-off radius of $r_c = 1.5\sigma$ (where σ is the atomic diameter) and corresponds approximately to the first local minimum in the radial distribution function. Applying such low cutoff to the truncated and shifted potential will lead to wrong physics and large energy drift⁷. The SF method therefore decreases the number of interactions significantly and thus the computational time. The potential corresponding to the SF interaction does however not match the original potential for $r < r_c$ from which the SF interaction was derived. Therefore, the thermodynamical properties can-

not be compared directly, but can be derived from perturbation theory^{2,7}.

For long-ranged interactions, like the Coulomb interaction, one cannot simply introduce a standard cut and shifted potential. For example, simply truncating and shifting the Coulomb potential produces spurious fluid structure and wrong dynamics⁸. Numerous attempts have been made to overcome this problem. For example it has been suggested to use smoothing functions, but this leads in general to poor results, see Refs. 9,10. Wolf *et al.*¹¹ cleverly showed that using a simple truncated and shifted Coulomb potential corresponds in practice to summing over interactions in a non-neutral sphere. To compensate for this these authors introduced a neutralizing term into the Coulomb potential; they further showed that faster convergence to the true energy is achieved by applying a damping factor α . The Wolf method is computationally much faster than the classical Ewald summation technique and is today widely used within the scientific simulation community. The choice of the damping factor, α , is, like the Ewald damping parameter^{2,12}, somewhat arbitrary, and the optimal value must be found by comparison with either experimental data or results from, e.g., the Ewald method^{10,13}. If the Wolf damping parameter α is zero, the Wolf method reduces to the SF approximation¹⁴, see also Denesyuk and Weeks¹⁵ for a discussion. We note that an SF method for the Coulomb interactions was used as a clever trick in the biochemical simulation community^{16,17} before the work by Wolf *et al.*

In this paper we apply the Wolf method in molecular dynamics simulations of a simple model of a molten salt and liquid water. In order to find the optimal value of the Wolf damping parameter α we compare the simulated thermodynamical, dynamical, and structural properties with previously published results¹⁸ based on the Ewald method. We show that the optimal value of α depends on the property one wishes to calculate and the cutoff distance used. This sets the stage for documenting the

main conclusion of this paper: for the systems studied here the SF approximation works as well as the Wolf method, confirming similar findings of Fennell and Gezelter¹⁴. Besides being conceptual simpler than the Wolf method, the SF method allows for more than a doubling of the computational speed.

II. THE WOLF APPROXIMATION TO THE COULOMB POTENTIAL

If r is the distance between two particles, the force acting on one particle from the other is $\mathbf{F}(r) = f(r)\mathbf{r}/r$, where f is for simplicity denoted the “force” and is minus the derivative of the corresponding potential function with respect to r . For the Wolf method¹¹ the force is given by

$$f_W(r; \alpha, r_c) = z_i z_j \left[\frac{\text{erfc}(\alpha r)}{r^2} - \frac{\text{erfc}(\alpha r_c)}{r_c^2} + \frac{2\alpha}{\sqrt{\pi}} \left(\frac{\exp(-\alpha^2 r^2)}{r} - \frac{\exp(-\alpha^2 r_c^2)}{r_c} \right) \right] \quad (1)$$

for $r < r_c$ and where $\text{erfc}(x) = 1 - \text{erf}(x)$ is the complementary error function. Here z_i and z_j are the charges of the two particles in question, r_c is the cutoff (i.e., $f_W = 0$ for $r \geq r_c$), and α is the Wolf damping parameter. In the paper by Wolf *et al.* it is implicitly understood that $\alpha r_c > 1$ such that the cutoff only takes effect beyond range of damping. The damping parameter was introduced in order to ensure faster convergence to the limiting Madelung energy¹¹. Unfortunately, there is no theoretical prediction for the optimal value of α , which must be found by comparison with other well-established methods like the Ewald summation method^{10,11,13}. Wolf *et al.*¹¹ and Demontis *et al.*¹³ have shown via molecular dynamics simulations that the Wolf method reproduces the results obtained by the Ewald summation method for $r_c \geq 5d_{ij}$, where d_{ij} is the distance between oppositely charged particles in the first coordinate shell. Demontis *et al.*¹³ also suggested that the optimal damping parameter is given by $\alpha = 2/r_c$ for sufficiently large systems.

From Eq. (1) it follows that for $\alpha \rightarrow \infty$ one has $f_W \rightarrow 0$, and that for $\alpha \rightarrow 0$ the force reduces to

$$f_{SF}(r; r_c) = z_i z_j (1/r^2 - 1/r_c^2) \text{ for } r < r_c. \quad (2)$$

This is the truncated and shifted force (SF) cutoff^{2,6}.

In Fig. 1(a) we plot the difference between the Wolf force, f_W , and the corresponding Coulomb force, $f_C = z_i z_j / r^2$, for different damping parameters. Clearly the damping parameter has a non-trivial effect on the force. For $\alpha = 0$ the difference is small compared to large values of α , suggesting that the SF cutoff, Eq. (2), gives a good approximation to the Coulomb interaction. From Fig. 1(a) it is seen that an optimal value of α exists that minimizes the difference. One way to identify this opti-

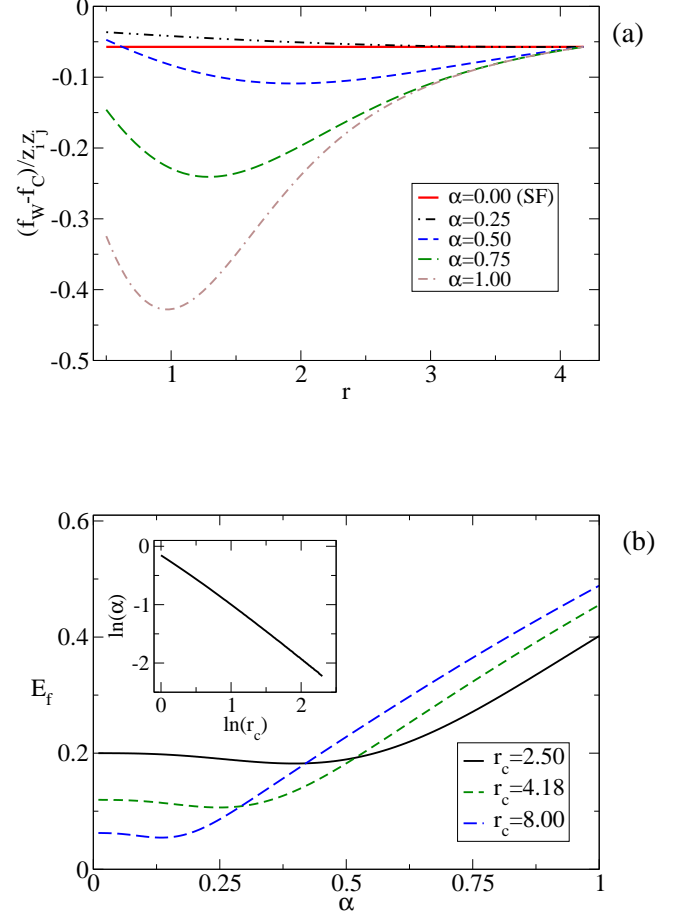


FIG. 1: [Color online] (a): Difference between the Wolf force, f_W , and the Coulomb force, f_C , for $\alpha = 0.0, 0.25, 0.5, 0.75$ and 1.0 . In all graphs the cutoff is given by $r_c = 4.18$. (b): The measure of the difference between the true Coulomb force and the Wolf force, E_f , defined in Eq. (3) plotted as a function of α for three different cutoffs. The inset shows the optimal value of α plotted as a function of r_c .

mal value is by minimizing the function

$$E_f(\alpha, r_c) = 1 - \frac{\int_0^{r_c} f_W(r; \alpha, r_c) dr}{\int_0^{r_c} f_C(r) dr}, \quad (3)$$

which measures the total relative difference between $f_W(r)$ and $f_C(r)$ such that $E_f \geq 0$ (since $f_W \leq f_C$ for all r). In Fig. 1(b) E_f is plotted for three different cutoff distances. The optimal Wolf damping parameter converges to zero as r_c increases, which reflects the simple fact that $f_W \rightarrow f_C$ for $r_c \rightarrow \infty$ and $\alpha \rightarrow 0$. More interestingly, the quantity E_f does exhibit very little difference between the optimal value of α and $\alpha = 0$. The

inset in Fig. 1(b) shows that the optimal Wolf parameter determined by the minimum of Eq. (3) is given roughly by $\alpha \approx 3/(4r_c)$. This simple analysis is consistent with the r_c dependence suggested by Demontis *et al.*¹³ based on molecular dynamics simulations (but they predict a smaller estimate of α by a factor of 3/8).

The conclusion from Fig. 1 is that setting $\alpha = 0$, i.e., adopting the SF approximation, gives results that are close to those obtained by carefully optimizing α . This and the recent work by Toxvaerd and Dyre⁷ motivate the below reported molecular dynamics simulations, which compare the Wolf method to the SF cutoff for other quantities and realistic systems. As “truth” we take the well-established, but computationally expensive, Ewald summation method.

III. RESULTS FOR THE HANSEN AND MCDONALD MOLTEN SALT MODEL

A series of molecular dynamics simulations was performed of a model molten salt proposed by Hansen and McDonald¹⁸. Briefly, in this two-component model the ions are simple spherical particles that interact via a Coulomb potential and a van der Waals type potential given by the inverse power law $\phi(r) = \frac{\epsilon^2}{n\sigma} \left(\frac{\sigma}{r}\right)^n$, where $n = 9$, ϵ defines the energy scale and σ is the usual Lennard-Jones length scale parameter¹. We refer the reader to the reference for the full details. In the simulations we applied the Wolf method and varied the cutoff between 2.5 and 8.0 σ . The simulation box used was twice the size of the cutoff whenever $r_c > 4.18\sigma$; for smaller cutoffs the box length was fixed to 8.36 σ . The number density for all systems were $\rho = 0.368\sigma^{-3}$, thus, the number of ions varied from 216 to 1508. The results presented below were found to be independent of system size. The temperature T is controlled using a Nosé-Hoover thermostat^{19,20} with $T = 0.0177\epsilon/k_B$. The results are compared to previously published data where the Ewald summation method was used¹⁸, which represent the “true” Coulomb interaction.

First, in Fig. 2 (a) we compare the total potential energy obtained from the Wolf method U_W for three different cutoff radii and varying damping parameters with the potential energy U_E from the Ewald summation method. We note that U_W is obtained directly from the Wolf potential function^{10,11} corresponding to the force given in Eq. (1). It is observed that U_W is within the statistical uncertainty equal to U_E for sufficiently small damping parameters, even for quite small cutoffs. This could lead to the conclusion that the Wolf method accounts correctly for electrostatic interactions for small cutoff distances. However, if one plots the radial distribution function g , Fig. 2(b), we see that for $r_c = 2.5\sigma$ the structure differs significantly from the result obtained using the Ewald summation method. This is true for all values of the damping parameter. From Fig. 2(b) we also notice that the SF approximation captures the structural prop-

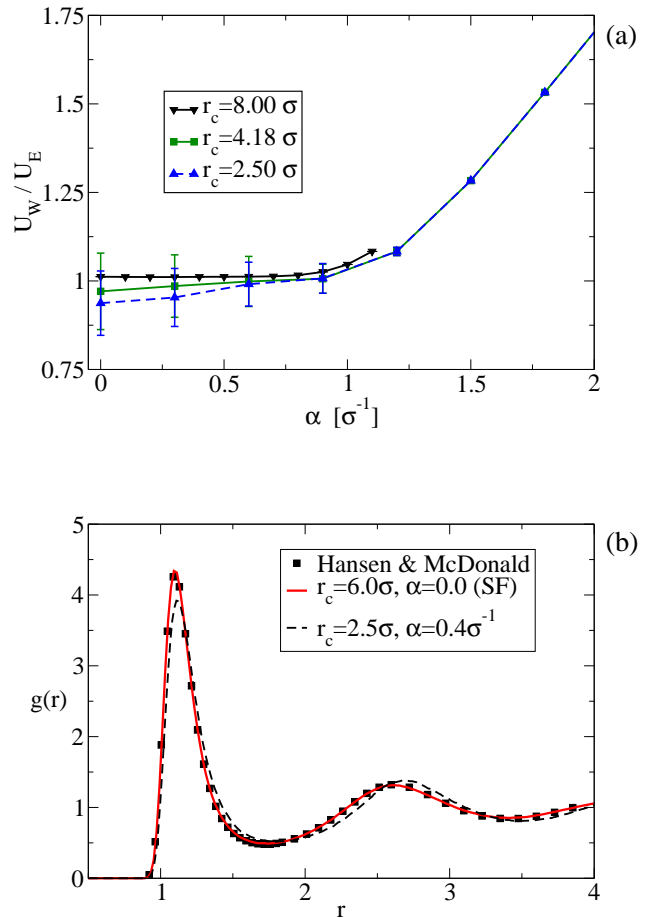


FIG. 2: [Color online] (a): Comparison of the potential energy of the Hansen-McDonald molten salt model for varying damping parameter. Error bars represent the standard error of ten independent runs. U_E is found in Ref. 18. (b): Radial distribution functions for unlike charged particles (lines) for $\alpha = 0$ (the SF approximation) and $r_c = 6\sigma$ and for $\alpha = 0.4\sigma^{-1}$ and $r_c = 2.5\sigma$. The filled black squares are data points taken from Ref. 18.

erties correctly for $r_c = 6\sigma$, which is the smallest cutoff distance meeting the Wolf *et al.*¹¹ and Demontis *et al.*¹³ criterion $r_c \geq 5d_{ij}$.

We study the radial distribution function dependence of r_c and α by defining the error parameter E_g via

$$E_g = \frac{\int_0^{r_c} |g_W(r) - g_E(r)| dr}{\int_0^{r_c} g_E(r) dr}, \quad (4)$$

where g_W is the radial distribution function for unlike charged particles of the Wolf method and g_E the radial distribution function produced by the Ewald summation method. Similarly, the following error parameter

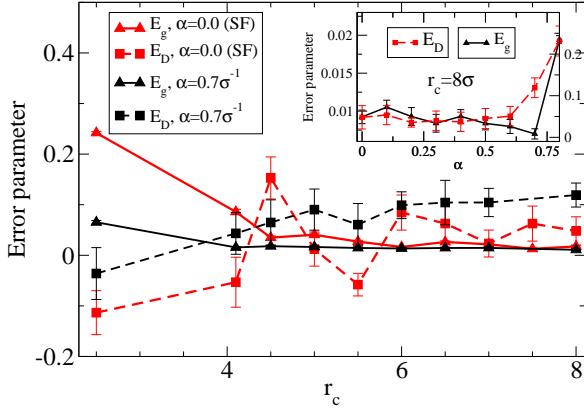


FIG. 3: [Color online] Error parameters as a function of cutoff for different damping parameter for the Hansen and McDonald molten salt system. The inset shows the error parameters for $r_c = 8\sigma$ as functions of α .

E_D quantifies the difference in diffusion constant

$$E_D = \frac{D_W}{D_E} - 1, \quad (5)$$

where D_W and D_E are the diffusion constants obtained from the Wolf and Ewald methods, respectively. Note that $E_g \geq 0$, whereas E_D can be negative. The “correct” radial distribution function, g_E , and diffusion constant, D_E , were taken from Ref. 18. Figure 3 shows the two error parameters for different cutoff radii and damping. The damping parameter $\alpha = 0.7\sigma^{-1}$ was chosen because E_g exhibits a minimum for this value for a large range of cutoffs. This is not the case for E_D , however, which features a minimum for lower values of the damping parameter, depending on the cutoff (as expected from Fig. 1 (b)). This inconsistency is illustrated in the inset in which the error parameters are shown for $r_c = 8\sigma$ as functions of α . Obviously, any $\alpha < 0.6\sigma^{-1}$ may be chosen to minimize E_D , whereas E_g features a minimum for $\alpha = 0.7\sigma^{-1}$. We note that $r_c = 8\sigma > 5d_{ij}$ and the cutoff radius fulfills the criterion defined by Wolf *et al.* and Demontis *et al.*

From Fig. 3 it is seen that E_g is relatively large for small cutoffs (as expected), but that it for non-zero damping parameters quickly decreases and reaches almost zero for $r_c > 4.0\sigma^{-1}$. For the SF approximation one needs $r_c > 6.0\sigma$ in order to obtain the same accuracy in the radial distribution function. For large cutoffs the SF approximation results in better diffusion constants than the Wolf method with $\alpha = 0.7\sigma^{-1}$. We could, of course, have optimized α with respect to the diffusion constant (giving $\alpha \cong 0.3\sigma^{-1}$ for a large range of cutoffs). This, however, would decrease the agreement for the radial distribution function. This fact is highlighted in Table I, where the error parameters are listed

$\alpha [\sigma^{-1}]$	E_D	E_g
0.0 (SF)	0.04 ± 0.02	0.017 ± 0.002
0.3	0.03 ± 0.01	0.019 ± 0.002
0.7	0.12 ± 0.02	0.010 ± 0.001

TABLE I: Error parameters, E_D and E_g , for different values of the damping parameter. $\alpha = 0.3\sigma^{-1}$ and $\alpha = 0.7\sigma^{-1}$ correspond to the optimized values with respect to diffusion and radial distribution function, respectively. $\alpha = 0.0\sigma^{-1}$ corresponds to the SF approximation.

for values of α optimized, respectively, with respect to the diffusion constant and the radial distribution function ($r_c = 8.0\sigma$). For comparison we also give the error parameters for the SF approximation. Within the statistical uncertainty there is no difference between the Wolf method using $\alpha = 0.3\sigma^{-1}$ and the SF approximation.

Up to this point we have only discussed the structural and diffusive properties in the long time limit. To compare the short-time dynamics of the two methods we plot the velocity autocorrelation function $C_{vv}(t)$ and the intermediate scattering function in Fig. 4. From Figs. 2 and 3 it was concluded that for small r_c ($r_c \approx 4.0\sigma$) and large α ($\alpha \approx 0.7$) both the potential energy and the radial distribution function are in excellent agreement with the Ewald summation method, but in Fig. 4 we clearly observe the short-time dynamics is not correct for this set of parameter values. This shows that the cutoff must be sufficiently large for the Wolf method to correctly account for all the fluid properties – but at such large cutoff the SF approximation may be applied instead since it results in the same accuracy.

IV. RESULTS FOR A WATER MODEL

We also tested the SF approximation for liquid water at the state point $(T, \rho) = (300 \text{ K}, 998 \text{ kg m}^{-3})$ using the flexible single point charge (SPC/Fw) water model²¹. In this model the chemical bond and the bending angle are allowed to vibrate around their zero-force values. The model is easy to implement and has been shown to predict many bulk properties better than for example the SPC, SPC/E and TIP3P models^{21,22}. In Fig. 5(a) we plot the oxygen-oxygen radial distribution function g_{oo} for the Wolf and SF methods. For comparison, data from Ref. 21 are shown (filled squares), where the Coulomb interactions were evaluated using the particle-mesh Ewald (PME) method²³. The radial distribution function is reproduced reasonably well by both methods. The SF approximation captures the liquid structure at least as well as the Wolf method, except at the first peak which is slightly underestimated. The radial distribution functions for both the SF and the Wolf methods are independent of the cutoff for radii larger than 9 Å, the value used by Zahn *et al.*¹⁰; this corresponds to

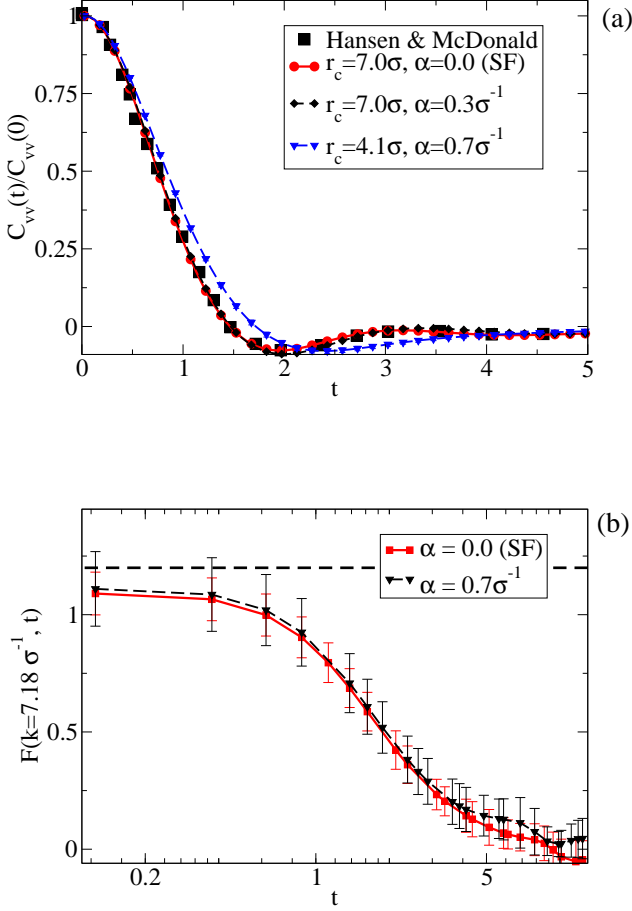


FIG. 4: [Color online] (a): Normalized velocity autocorrelation function for the Wolf and the SF methods. Only the short time data are shown. The error bars are comparable to the size of symbols. (b): Coherent intermediate scattering function for wave-length $k = 7.18\sigma^{-1}$ and $r_c = 7.0\sigma$. The horizontal line is the interpolated value of the static structure factor $S(k) = F(k, 0)$ taken from Ref. 18. The time t is given in standard reduced molecular dynamics units.

$r_c \approx 5d_{ij}$ since the oxygen-hydrogen distance is around 1.8 \AA . In Fig. 5(b) the center-of-mass velocity autocorrelation function is plotted for two different cutoffs for both methods. This dynamic property is largely independent of method and cutoff, as is the case for the liquid structure. The same conclusion was reached by Fennell and Gezelter¹⁴. For the SF approximation we obtain a diffusion constant of $2.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and a shear viscosity of $0.78 \times 10^{-3} \text{ Pa s}$. This can be compared with the experimental values $2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $0.85 \times 10^{-3} \text{ Pa s}$. It is also worth mentioning that Zahn *et al.*¹⁰ used $\alpha = 0.06\sigma^{-1}$ in their simulations of (rigid) SPC/E water, but found that the potential energy was in better agreement with the Ewald method for even lower damping

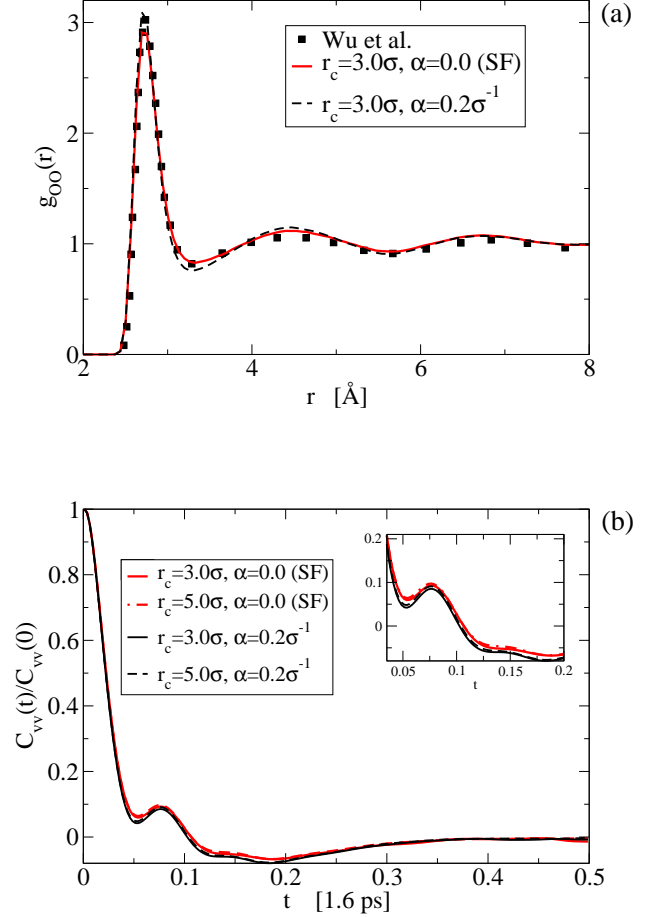


FIG. 5: [Color online] (a): Oxygen-oxygen radial distribution function for the SPC/Fw water model using SF and Wolf methods. The squares represent data taken from Ref. 21. (b): Normalized center-of-mass velocity autocorrelation functions. The inset shows a zoom of the time interval 0.065 to 0.32 ps. In both (a) and (b) $\sigma = 3.16 \text{ \AA}$.

parameters. For $\alpha = 0.06\sigma^{-1}$ we observe no difference to the SF approximation.

V. CONCLUDING REMARKS

In conclusion, for simple molten salts and liquid water the SF approximation reproduces various properties as well as the Wolf method. The Wolf method has one more parameter than SF, and consequently this method may be optimized to give slightly better agreement with the Ewald summation method. Such an optimization, however, must be carried separately out for each property in focus and for each different system. Beside its simplicity (and thus easy-to-code feature), we found that

the SF approximation leads to a simulation speed-up of 2-3 compared to the Wolf method. Of course, the actual speed-up depends on the specific problem and the use of optimization techniques, but the calculation of the four terms in Eq. (1) involves complicated mathematical functions and is deemed to consume considerably more computational resources than the simple SF approximation. We wish to stress here that the paper of Wolf *et al.* was the first to correctly analyze why the SF approximation for Coulomb forces is superior to the standard truncated and shifted potential interaction model.

Fennell and Gezelter¹⁴ carefully analyzed an impressive number of different systems including simple crystals showing a good agreement between the SF method and the Ewald technique. In their conclusion the authors suggested that the SF approximation can also be used for confined geometries, thereby overcoming the enforced periodicity in the unmodified Ewald method. We

agree that the Ewald method can be problematic (even for periodic systems²⁴), but, the SF approach (as well as the Wolf method) is an approximation that suppresses the intrinsic long-ranged nature of the Coulomb interactions leading to an artificially molecular orientation^{8,25} in confinements. For confined fluids alternative methods have recently been advised, see Refs. 15,26,27.

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